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ORIGINAL CONTRIBUTION

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Styrene and methylmethacrylate oil-in-water microemulsions

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Abstract A simple procedure for the preparation of styrene-in-water and methylmethacrylate (o/w) microemulsions was established. This consisted of the preparation of a w/o emulsion using a low HLB number surfactant (Synperonic NP4, nonyl phenyl with 4 mol ethylene oxide) and a small amount of an anionic surfactant (Aerosol OT, diethyl hexyl sulphosuccinate, or sodium dodecyl benzene sulphonate). The w/o emulsion was then titrated with an aqueous solution of a high HLB number surfactant (Synperonic NP15, nonyl phenyl with 15 mol ethylene oxide). The droplet size and polydispersity were determined using photon correlation spectroscopy (PCS). The temperature range within which a microemulsion remained stable decreased with increase in the concentration of styrene or methylmethacrylate and this could be explained in terms of the phase diagram of the microemulsion system. Conductivity measurements as a function of temperature showed that the systems are oil-in-water microemulsions.

Key words Styrene – methylmethacrylate – oil-in-water microemulsions – anionic surfactant

Introduction

In recent years, there has been considerable interest in the use of nanoparticles (<50 nm) for medical applications, e.g. in targeted delivery of drugs, in transport through membranes, in diagnostics, etc. [1]. One of the most convenient methods for the preparation of nanoparticles is by using an oil-in-water (o/w) microemulsion of the monomer [2]. Provided the conditions are well controlled during the polymerization process, it is possible to obtain nanoparticles that have a comparable size to those of the microemulsion droplets. In this paper, we will describe a simple procedure for preparation of styrene and methylmethacrylate (MMA)-in-water microemulsions based on nonionic surfactants. The latter are convenient for preparation of o/w microemulsions and they do not require the addition of an alcohol (cosurfactant) which could be detrimental during the polymerization process [3].

One of the earliest and a simple method for preparation of microemulsions was developed by Schulman and coworkers [4, 5]. An o/w emulsion was firstly prepared using an anionic surfactant such as potassium oleate which was then titrated by a medium chain alcohol such as pentanol or hexanol. The first addition of the alcohol produced little change in the o/w emulsion but by gradually increasing the alcohol, the system produced a gel of a lamellar liquid crystalline structure. At this point, further small addition of the alcohol caused inversion producing a transparent w/o microemulsion. This inversion process could have been easily predicted from consideration of the phase diagram [5] of the system as well as the change in the packing parameter, *P*, of the surfactant molecules [6]. *P* is given by the ratio of v/al, where v is the volume of the alkyl chain and l its length and a is the cross-sectional area of the head group. With potassium oleate, $P < 1$, since the ionized head group has a much larger cross-sectional area than that of the hydrocarbon chain and the surfactant produces an o/w emulsion. On addition of the alcohol, P gradually increases and finally becomes greater than 1, producing a w/o microemulsion. We have adopted an inverse procedure similar to that of Schulman and coworkers in order to produce an o/w microemulsion. A w/o emulsion was first prepared using a surfactant with a low hydrophilic–lipophilic balance (HLB) number which was then titrated with an aqueous solution of a second surfactant with a high HLB number. The system also passed through a gel phase after which further addition of the solution of the high HLB surfactant caused inversion to an o/w microemulsion. As mentioned above, we used nonionic surfactants to avoid any complication during the polymerization process which was to follow. As we shall see later, it was found necessary to add a small amount of an anionic surfactant to facilitate the inversion process and production of the microemulsion.

Experimental

Materials

Styrene and methylmethacrylate were supplied by BDH, both were 99.5% grade and were used as received. Nonyl phenol polyethylene oxide surfactants (Synperonic NP) were supplied by ICI Surfactants. Two molecules containing 4 and 15 mol ethylene oxides (Synperonic NP4 and NP15, respectively) were used. Sodium diethyl hexyl sulfosuccinate (Aerosol OT), 99% grade, was purchased from ALDRICH and was further purified by making a carbon-black slurry of a methanol solution of the surfactant, followed by filtration [7]. Sodium dodecyl benzene sulfonate (NaDBS), 80% w/w solution in water, was supplied by Albright & Wilson (80% w/w solution in water) and was used without further purification. Water was doubly distilled using an all glass apparatus.

Preparation of oil-in-water microemulsions

The experimental procedure first consisted in the preparation of a w/o emulsion by slowly adding water to an oil solution of the low HLB surfactant (Synperonic NP4) and the ionic surfactant (AOT and NaDBS for styrene and MMA microemulsions, respectively), while stirring (using a magnetic stirrer). Secondly, the w/o emulsion was titrated using a 15% (w/w) aqueous solution of the high HLB surfactant (Synperonic NP15). The emulsion remained milky until the gel phase was reached, when it suddenly became viscous and transparent. At that point further addition of the surfactant solution caused inversion, producing an oil-in-water microemulsion. For this procedure to succeed, it was essential to produce stable emulsions as a starting system. This could be obtained using NP4 and the ionic surfactants.

Characterization of the microemulsions

Photon Correlation Spectroscopy (PCS)

Measurements were carried out using a MALVERN 4700 PCS instrument. An Argon laser beam at a wavelength of 488 nm was used and the intensity of the scattered light was measured at an angle of 90°. In this procedure, one measures the fluctuations of the intensity of the scattered light using a photon correlator. From the intensity fluctuations, the diffusion coefficient D of the particles is obtained and is used to calculate the hydrodynamic radius, R_h, from the Stokes–Einstein equation [8],

$$D = \frac{kT}{6\pi\eta R_h}, \qquad (1)$$

where k is the Boltzmann constant, T the temperature and η the viscosity of the continuous phase.

The above method is suitable for dilute dispersions of monodisperse particles, in which case a single exponential of the autocorrelation function $g^{(1)}$ as a function of delay time τ is obtained. In this case, one can simply calculate D from the slope of the log $g^{(1)}$ vs. τ curve. However, in our case, the microemulsion was polydisperse and concentrated [8]. In the case of concentrated dispersions like microemulsions, the hydrodynamic radius obtained by PCS may be corrected using the following relationship [9] which gives the collective diffusion coefficient D as a function of its value at infinite dilution D_0,

$$D = D_0(1 + \alpha\phi), \qquad (2)$$

where α is a constant that is equal to 1.5 for hard spheres with repulsive interaction and ϕ the volume fraction of oil.

Conductivity

These measurements were carried out using a Wayne Kerr Universal Bridge at a frequency of 1 kHz. A dipping cell having platinum electrodes was used; the cell constant was equal to 1.41 cm^{-1}, which was previously determined using standard KCl solutions. The temperature was varied by means of a thermostatically controlled bath which circulated ethylene glycol/water and was determined with an accuracy of ±0.1 °C.

Results and discussion

Styrene-in-water microemulsions

Microemulsions containing up to 18% styrene could be prepared using the inversion procedure described in the experimental section. The amount of Synperonic NP4, Synperonic NP15 and Aerosol OT (AOT) depended on the monomer content. Figure 1 shows the variation of the concentration of AOT, Synperonic NP4 with the percentage of styrene, whereas Fig. 2 shows the corresponding variation of NP15 and water. It can be seen from these figures that as the amount of styrene in the microemulsion increases, the percentage of AOT and Synperonic NP4 increases, whereas that of NP15 decreases. The linear relationships shown in Figs. 1 and 2 could be represented by the following regression equations,

$$y_1 = 0.007x - 0.014 , \quad (3)$$

$$y_2 = 0.112x + 0.183 , \quad (4)$$

$$y_3 = -0.448x + 73.67 , \quad (5)$$

$$y_4 = -0.912x + 84.96 , \quad (6)$$

where y_1, y_2, y_3 and y_4 are the wt% of AOT, NP4, NP15 and water, respectively.

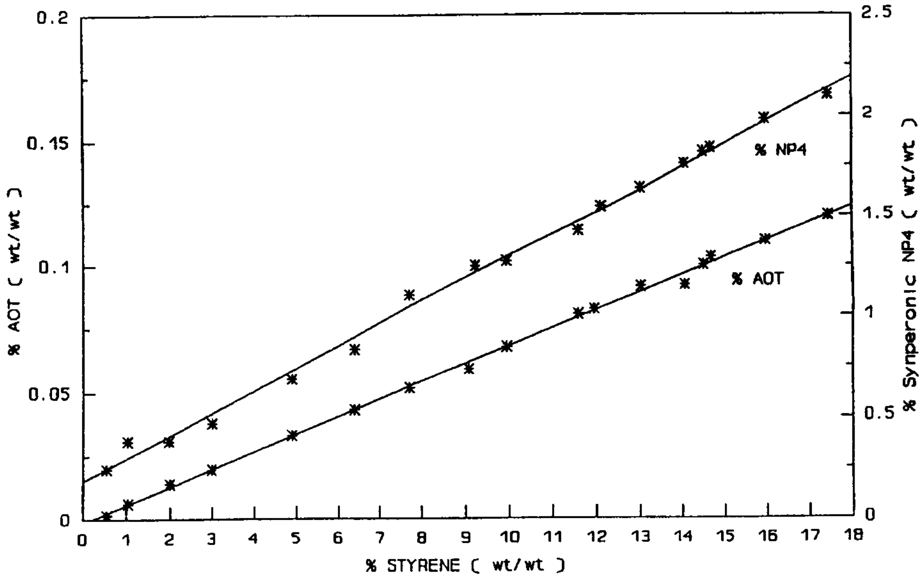


Fig. 1 Composition of styrene-in-water microemulsions, showing the variation of percentage AOT and NP4 with the oil concentration

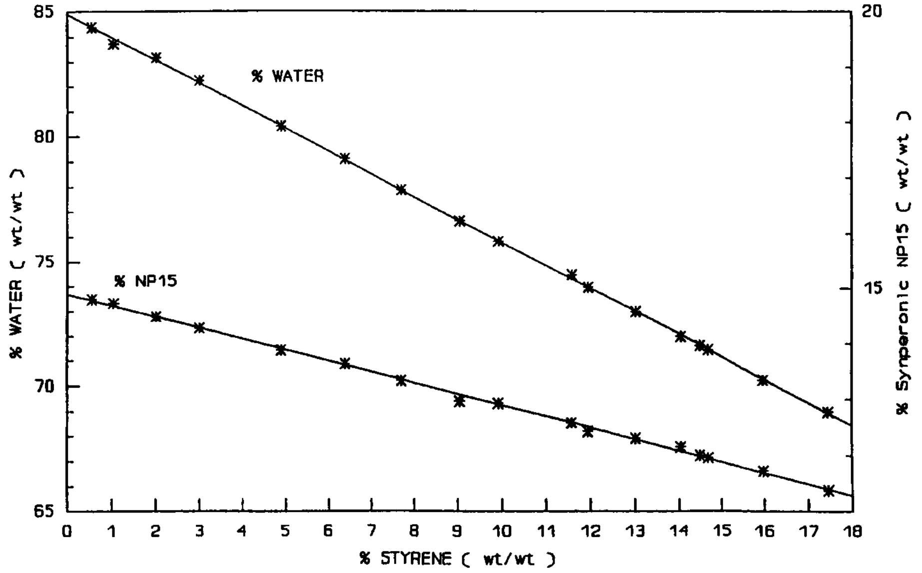


Fig. 2 Composition of styrene-in-water microemulsions, showing the variation of percentage of NP15 and water with the oil concentration

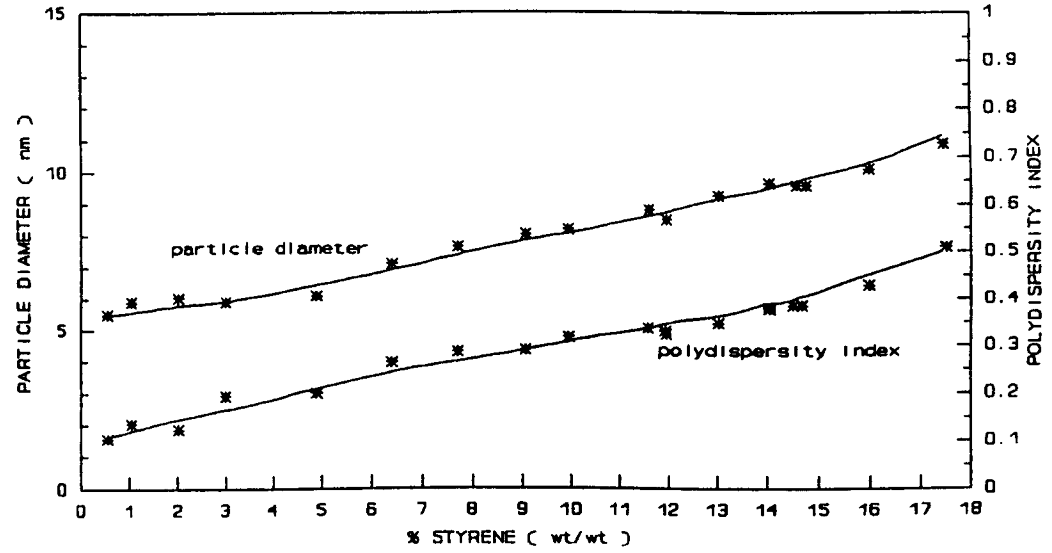


Fig. 3 Droplet diameter and polydispersity index vs. styrene concentration for styrene-in-water microemulsions

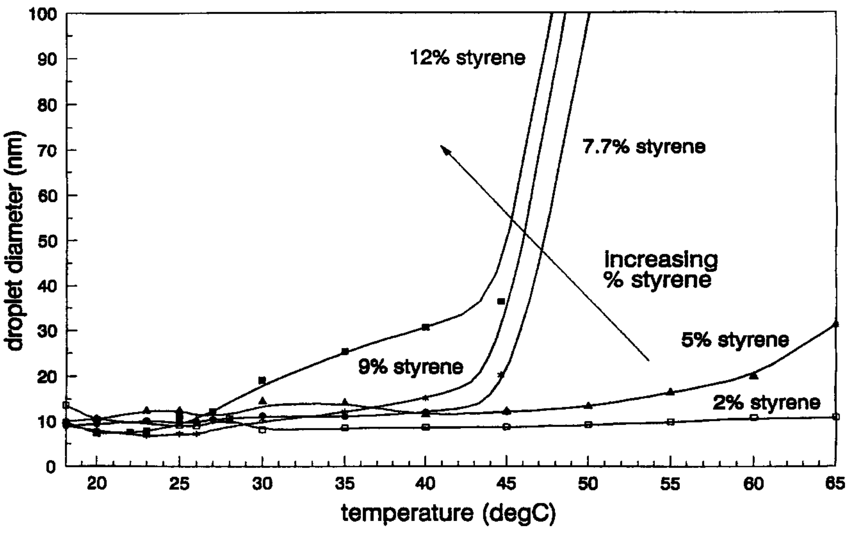


Fig. 4 Variation of droplet diameter of styrene-in-water microemulsions with temperature

Figure 3 shows the variation of the apparent hydrodynamic diameter and polydispersity index of the microemulsions as a function of the styrene content. Correction of the radius due to the effect of volume fraction, according to Eq. (5), leads to a small increase in *d* and therefore it was decided to plot the apparent diameter in all the results given in this paper. The results of Fig. 3 show a gradual increase in *d* and polydispersity index with increase in styrene content. This is consistent with the decrease in the ratio of surfactant to monomer concentration as the latter is gradually increased.

It was found that the above microemulsions could then be prepared by mixing all the components at the right composition, i.e. without adopting the inversion technique. In all cases, the droplet diameter was similar to that in systems prepared using the titration method.

Figure 4 shows the variation of apparent diameter of the microemulsion with temperature at various styrene concentrations. Below 5% styrene, the microemulsions showed very small increases in diameter with increase of temperature up to 65 °C. Above 5% styrene, there was a rapid increase in droplet diameter above a critical temperature. This critical temperature decreased with increase in styrene concentration. These results can be explained by considering the phase diagram of systems based on nonionics [10]. Plots of temperature vs. oil concentration show the microemulsion region to be located between the solubilization and cloud-point curves.

At low oil content, the solubilization and cloud-point temperatures are separated from each other by several degrees and, hence, the microemulsion stability domain occurs over a wide temperature range. This explains the constancy of the droplet size with temperature (up to 65 °C) when the styrene concentration is lower than 5%. As the oil content of the microemulsion is increased, the solubilization temperature becomes closer to the cloud-point temperature and the stability domain of the microemulsion is reduced. This trend continues until the two temperatures become identical, at which value of the oil concentration no single isotropic microemulsion system is produced and the system tends to separate into several layers of oil, water and surfactant. The above trends can also explain why a microemulsion containing more than 18% styrene could not be formed at room temperature. In this case, the cloud-point temperature will be lower than ambient.

Figure 5 shows the variation of conductivity with temperature for microemulsions prepared using various amounts of styrene. All systems had high conductivities, indicating that they are o/w microemulsions. The conductivity shows a monotonic increase with increase of temperature but there was no sharp transition at the temperature where the droplet diameter showed a sharp increase (see Fig. 4). This may be accounted for by the presence of the ionic surfactant. The rapid increae in droplet diameter at a critical temperature may be accompanied by a change in the conductivity of the system. However, this change is relatively small and could not be detected with such highly conducting systems containing an ionic surfactant.

Methylmethacrylate-in-water microemulsions

Microemulsions containing up to 23% of methylmethacrylate (MMA) could be prepared using the titration method. The amount of sodium dodecyl benzene sulfonate (NaDBS), Synperonic NP4 and Synperonic NP15

Fig. 5 Variation of conductivity of styrene-in-water microemulsions with temperature

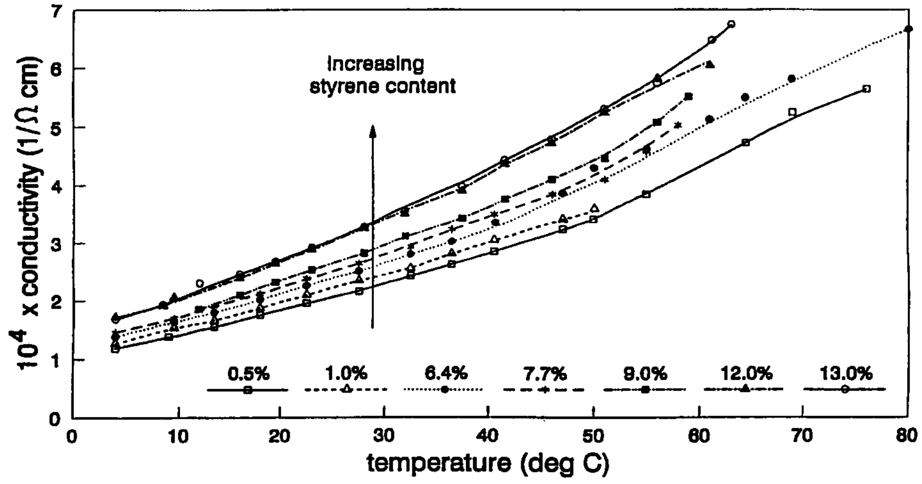
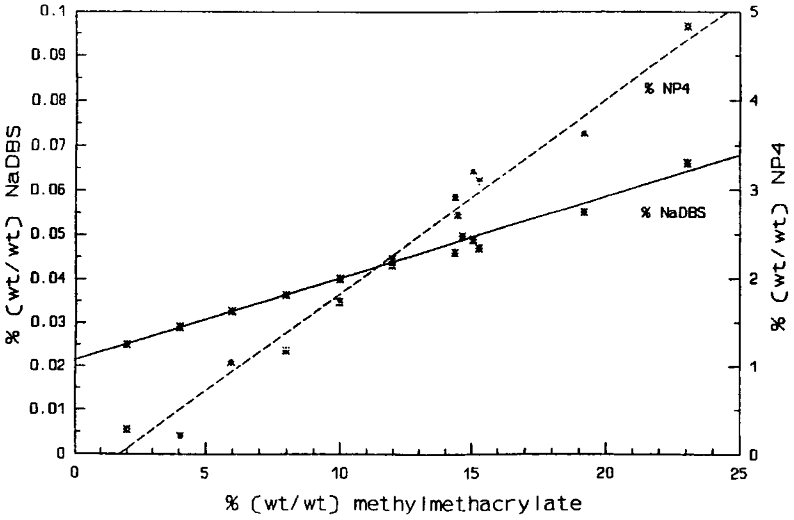


Fig. 6 Composition of methylmethacrylate-in-water microemulsions, showing the variation of the percentage of NaDBS and NP4 with the oil concentration



depended on the amount of monomer contained in the system. Figure 6 shows the variation of NaDBS and Synperonic NP4 as a function of the MMA concentration, whereas Fig. 7 shows the corresponding variation of Synperonic NP15 and water. From these graphs, it is clear that when the MMA content of the micro emulsion is increased the wt% of NaDBS and Synperonic NP15 increases, where the wt% of Synperonic NP15 decreases. The linear variations represented in Figs. 6 and 7 could be represented by the regression equations below,

$$y_1 = 0.0018x + 0.0214\ , \tag{7}$$

$$y_2 = 0.2192x - 0.3732\ , \tag{8}$$

$$y_3 = -0.2207x + 14.8972\ , \tag{9}$$

$$y_4 = 0.9996x + 85.4323\ , \tag{10}$$

where y_1, y_2, y_3 and y_4 are the wt% of NaDBS, NP4, NP15 and water, respectively.

At ambient temperature, one could prepare MMA-in-water microemulsions containing more monomer than in the case of styrene-in-water microemulsions. This shows that the MMA concentration at which the could point temperature and the solubilization temperature meet is higher than it is for styrene-in-water microemulsions. The temperature stability domain of the MMA-in-water microemulsions is therefore larger than in the previous case.

In Fig. 8, the variations of the hydrodynamic apparent diameter and the polydispersity index are represented as functions of the MMA content. The droplet diameter and the value of the polydispersity both increase slightly as the monomer content is increased. This is again in accordance with the decrease of the ratio of surfactant to

Fig. 7 Composition of methylmethacrylate-in-water microemulsions showing the variation of the percentage of NP15 and water with the oil concentration

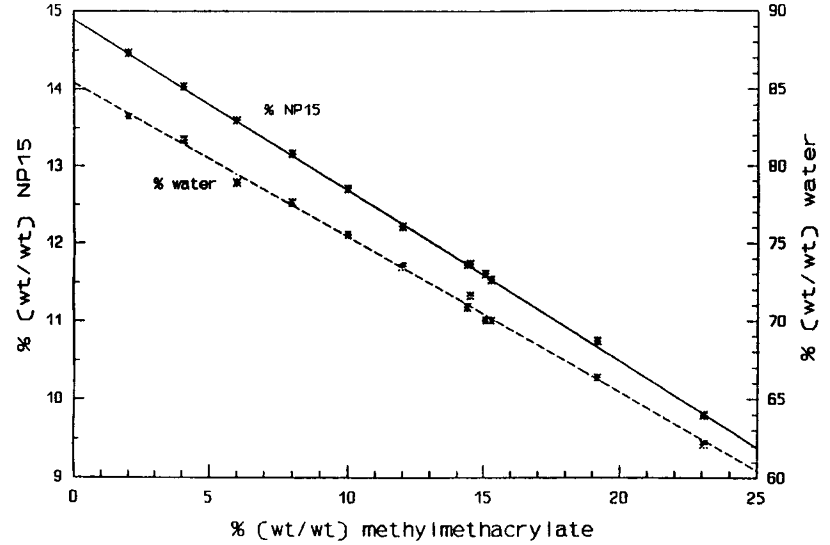
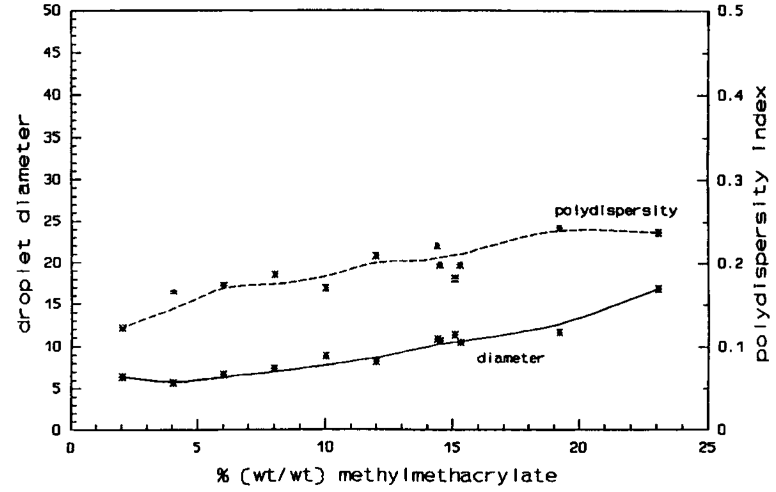


Fig. 8 Droplet diameter and polydispersity index vs. methylmethacrylate concentration for methylmethacrylate-in-water microemulsions



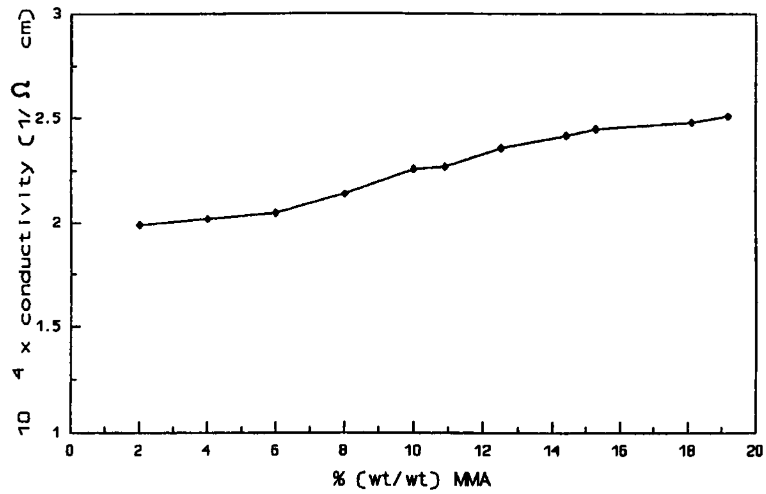


Fig. 9 Variation of conductivity with oil concentration for methylmethacrylate-in-water microemulsions

monomer concentrations when one increases the monomer content in the microemulsion. Figure 9 shows the variation of the conductivity versus methylmethacrylate concentration. The conductivity values indicate the presence of water-continuous systems. The conductivity increases slowly with increase of MMA. This can be easily correlated with the increase of the amount of ionic surfactant when the monomer content in the microemulsion is increased.

Conclusions

A simple procedure for the preparation of oil-in-water (o/w) microemulsions, whereby the oil is a monomer of styrene or methylmethacrylate, was established. A w/o emulsion was prepared using a low HLB surfactant (e.g. Synperonic NP4, nonyl phenyl with 4 moles ethylene oxide) and a small amount of an anionic surfactant (e.g. Aerosol OT, sodium diethyl hexyl sulphosuccinate, or sodium dodecyl benzene sulphonate. This w/o emulsion was then titrated with an aqueous solution of a high HLB surfactant (e.g. Synperonic NP15, nonyl phenyl with 15 mol ethylene oxide). A gel phase is produced after which further addition of the high HLB number surfactant solution caused an inversion to an o/w microemulsion. The microemulsions remained stable within a temperature range that decreased with increase in the monomer content.

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